

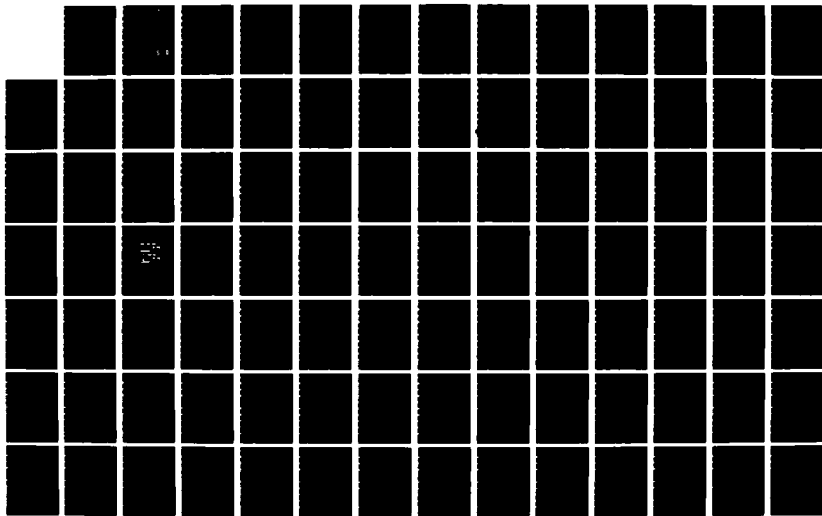
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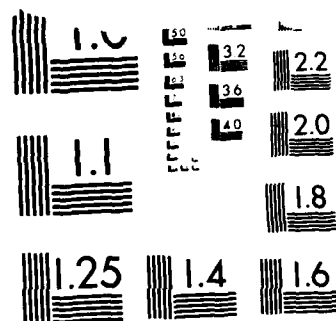
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A Review of Atmospheric Ozone and
Current Thinking on the Antarctic Ozone Hole

A thesis submitted in partial satisfaction of the
requirements for the degree Master of Science
in Atmospheric Science

by

Randolph Antoine Fix

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ABSTRACT OF THE THESIS

A Review of Atmospheric Ozone and Current Thinking on the Antarctic Ozone Hole

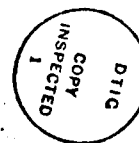
by

Randolph Antoine Fix

Master of Science in Atmospheric Science
University of California, Los Angeles, 1987

Professor S. V. Venkateswaran, Chair


A general review of the formation, global distribution and concentration variations on different temporal scales of atmospheric ozone is presented. The nature and extent of the recently discovered Antarctic ozone hole is discussed and summaries of the various theories that have been advanced to account for this phenomenon are reviewed.

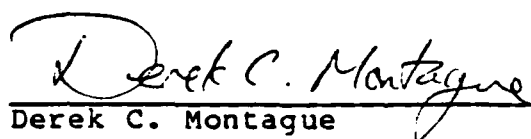


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The thesis of Randolph Antoine Fix is approved.


Carlos R. Mechoso


Derek C. Montague


S. V. Venkateswaran, Committee Chair

University of California, Los Angeles

1987

To my lovely wife, Diane

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CHAPTER I

INTRODUCTION

Although a trace constituent, ozone is of considerable importance to the radiation and heat balance of the earth's atmosphere. It protects the biosphere from the sun's deadly ultraviolet radiation. It also controls the thermal structure of the stratosphere thereby exercising a considerable control on the earth's climate. Events in the last two decades have produced an increased awareness of ozone's importance especially since the recognition that human activities can significantly disturb the ozone layer.

Ozone is a highly reactive molecule and certain chemical species in the stratosphere can diminish the ambient concentrations of ozone by increasing its rate of destruction. Since the 1970's, concern over increased ozone destruction by some of these species introduced into the stratosphere by man's activities has been an active scientific issue. The consequent increased flux of solar ultraviolet radiation incident on the earth's surface is known to have far-reaching consequences.

Ozone is also a highly variable constituent of the atmosphere, with pronounced day-to-day variations as well as seasonal changes. This characteristic of ozone makes detection of any influence on its concentration resulting from chemical contamination extremely difficult.

However, measurements of ozone in the Antarctic have revealed a dramatic decrease of the spring ozone values since 1979. While no clear link between man-made pollutants and this ozone depression or hole has been established, this is the first pronounced decrease of ozone that many scientists believe may be indicative of such a link.

This thesis is a discussion on atmospheric ozone, particularly ozone in the stratosphere. The photochemical formation of ozone is briefly described and observations of ozone resulting from several observational techniques are presented. Ozone distribution in the natural stratosphere is also discussed as well as the various processes which upset or perturb the natural ozone balance. Finally, observations and current thinking of the Antarctic ozone hole are summarized.

CHAPTER II

FORMATION OF THE OZONE LAYER

Ozone is present throughout the earth's atmosphere from the surface up to at least 100 km. In the mesosphere (>60 km), densities of ozone are quite low. The largest concentrations lie in the stratosphere at about 25 km. Concentrations of ozone in the troposphere are also less than the stratosphere, but can still play an important role in the chemical and radiation balance of the lower atmosphere.

Ozone is indeed the most important atmospheric constituent which absorbs ultraviolet solar radiation. Ultraviolet (UV) radiation is the part of the electromagnetic spectrum with wavelengths under 400 nanometers (nm). The UV portion of the spectrum is conventionally divided into three parts:

UV-A - 300 nm to 400 nm

UV-B - 220 nm to 300 nm

UV-C - 190 nm to 220 nm.

Since the energy of a photon of light is inversely proportional to its wavelength, photons in this part of the spectrum have larger amounts of energy than in the visible region of the spectrum. Wavelengths less than 320 nm have sufficient energy to damage DNA and RNA, the molecular building blocks of living cells, both strong absorbers of UV radiation below 300 nm (NRC,1983). Ozone

absorbs 99% of this energy, protecting plant and animal life from exposure to this harmful radiation. The absorption of solar radiation due to the presence of ozone and other naturally occurring atmospheric gases is depicted by the hatched areas in Fig. 1.

Ozone formation begins by the photodissociation of molecular oxygen at altitudes of 40 to 100 km. Photolysis occurs when molecular oxygen absorbs photons with energy in wavelengths of 130-175 nm (Schuman-Runge continuum), 175-210 nm (Schuman-Runge bands) and 215-240 nm (Herzberg bands and continuum). Absorption of photons in the Schuman-Runge bands and continuum is the dominant source of atmospheric odd oxygen at altitudes greater than 60 km. Photodissociation of O_2 in the Herzberg continuum is the dominant source of odd oxygen below 60 km.

The end products of the photolysis of O_2 are two highly reactive oxygen atoms whose lifetime is dependent on the density of third bodies and of molecular oxygen, O_2 . At altitudes of ~ 100 km, the lifetime of atomic oxygen is long due to this density dependence. However, once transported downward to the upper stratosphere, where the densities of third bodies and molecular oxygen are high, it combines very rapidly with an oxygen molecule through a collisional process to form ozone, O_3 . Referred to as the Chapman mechanism, after the well-known geophysicist who

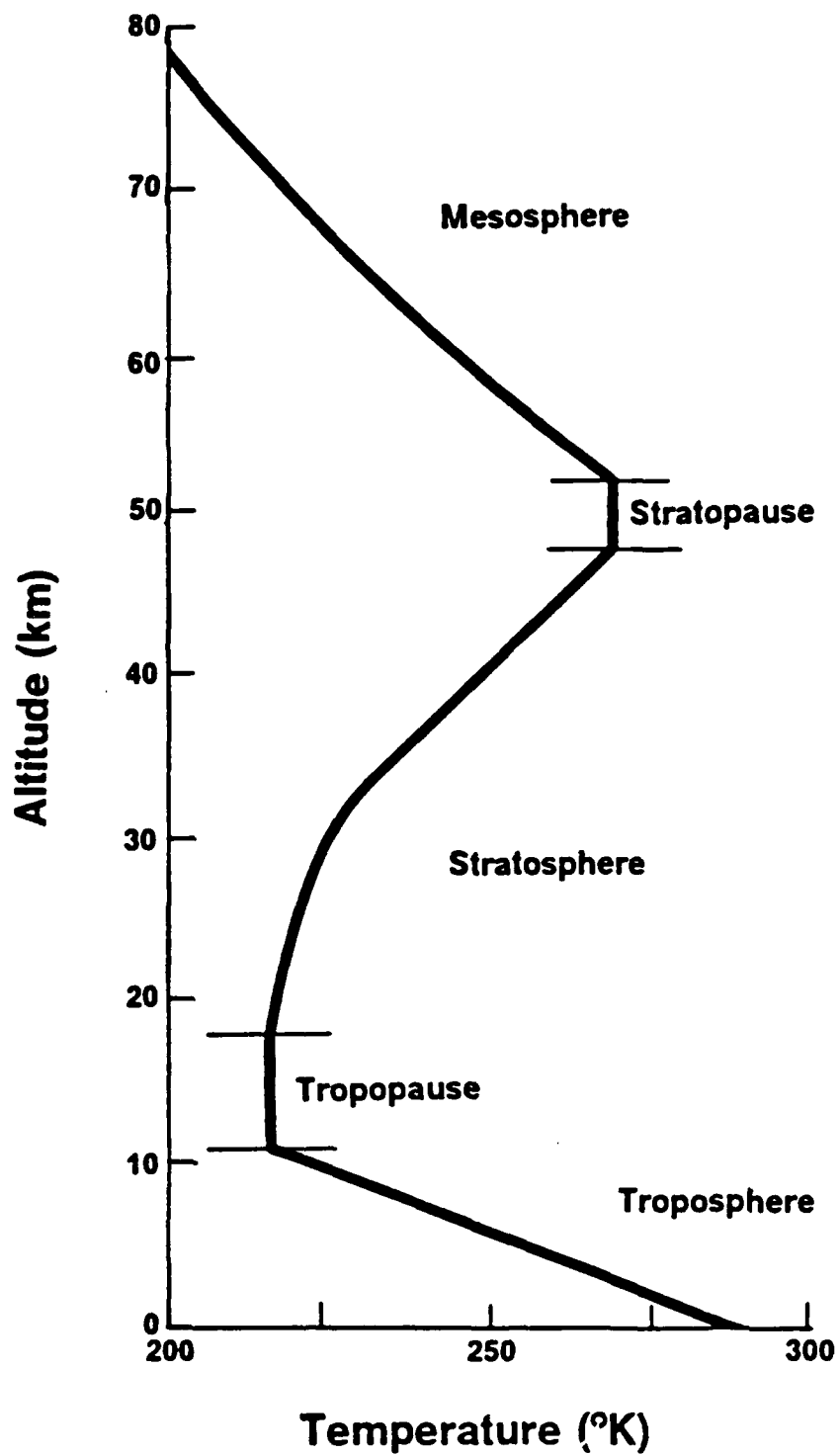
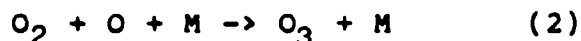


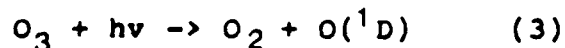
FIGURE 2. The thermal structure of the atmosphere.

first proposed these processes (Chapman, 1930), the chemical reactions are written:



where M indicates the third body and $h\nu$ represents one quantum of energy (h is Planck's constant and ν is the frequency of the absorbed light). The photolysis of molecular oxygen essentially absorbs all of the UV-C radiation, thus no radiation of wavelengths less than 220 nm reaches the earth's surface.

Absorption of incoming solar radiation by ozone occurs in the strong Hartley bands of wavelengths less than 308 nm, the weaker, temperature dependent Huggins bands which extend to longer wavelengths out to near 360 nm and the Chappuis bands which lie in the visible from 410 nm to 850 nm. Absorption in the Hartley region is by far the strongest and peaks close to 255 nm with an absorption cross section of about $1.2 \times 10^{-17} \text{ cm}^2$. The absorption is accompanied by the photodissociation process:



where $\text{O}(^1\text{D})$ represents a singlet oxygen atom in the first excited state. This free oxygen atom quickly combines with molecular oxygen through reaction (2) to form another ozone molecule. At wavelengths greater than about 310 nm the vibrational structure of the Huggins bands becomes

pronounced and the absorption cross section displays a significant temperature dependence. Ozone absorbs weakly in the visible region of the spectrum via the Chappuis bands that extend from 408 nm and peak near 600 nm with a cross section close to $5 \times 10^{-22} \text{ cm}^2$. Absorption in these two bands as well as wavelengths up to about 1100 nm (Craig, 1950) produces only ground state oxygen atoms, $\text{O}(^3\text{P})$, which also combine with molecular oxygen to form ozone. The altitudes and regions of the spectrum in which these processes take place are summarized in Table 1.

Through these processes, the trace amounts of ozone found in the stratosphere are capable of absorbing virtually all solar ultraviolet radiation. The absorbed solar energy in the UV is converted to thermal energy and is responsible for the existence of the stratosphere's positive temperature gradient. The maximum rate of energy input per unit mass of ozone occurs at 45 to 50 km and delineates the region of temperature maximum called the stratopause. Between the stratopause and the tropopause, which is the region of temperature minimum between 10 to 15 km, is the stratosphere which is characterized by a temperature inversion and dynamically stable air. Consequently, ozone has a role in determining stratospheric and tropospheric weather and climatic interactions. Figure 2 shows the thermal structure of the atmosphere.

Maximum production of ozone occurs in the equatorial upper stratosphere based on this photochemical theory. The combination of the approximately exponentially decreasing partial pressure of oxygen with the increasing solar flux density as the altitude increases results in maximum photodissociation rates of oxygen in this region of the atmosphere. Ozone, therefore, forms most rapidly at this level in the atmosphere. As we shall see, dynamical and chemical processes determine the latitude and altitude of maximum ozone concentrations.

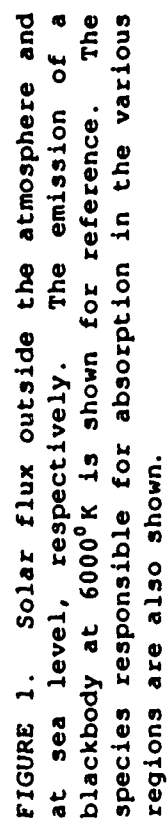


TABLE 1
ATTENUATION OF SOLAR ULTRAVIOLET
RADIATION THROUGH THE ATMOSPHERE

Wavelength Regions				Altitude	Region
120-200 nm	200-290 nm	290-320 nm	320-350 nm		
O ₂ absorbs almost completely	190-210 nm Absorption by O ₂ appreciable absorption by O ₃ appreciable	O ₃ absorption not important		Above 60 km	THERMO-SPHERE - 85 km
	No radiation penetrates below 11 km	O ₃ absorption attenuates more than loss by scattering	O ₃ absorption significantly attenuates radiation	60-33 km	MESO-SPHERE - 50 km
		Appreciable penetration through "atmospheric window"	40% of radiation penetrates to sea level	33-11 km	STRATO-SPHERE - 11 km
				11 km to sea level	TROPO-SPHERE

Source: Howard et al., 1960

CHAPTER III

TOTAL OZONE

3.1 Measuring Total Ozone

A number of different units are used in expressing the concentration of ozone in the atmosphere. Number mixing ratio is given by the number of molecules of the gas in, say, a million (10^6) molecules of air and is expressed as parts per million (ppm). Units of parts per billion (ppb) and parts per trillion (ppt) are also commonly used. Mass mixing ratio is given by the gas mass density over the air density and expressed as parts per million by mass (ppmm) or micrograms (10^{-6}) of the gas per gram of air ($\mu\text{g/g}$). Still another unit of gas concentration is the number density which is the number of molecules, atoms, or radicals present in a given volume of air, usually a cubic centimeter. Similarly, the mass density is the mass per unit volume. The partial pressure of a trace gas is usually expressed in nanobars (nb). All these units are used to express ozone concentrations, but the standard unit of ozone measurement is the Dobson unit (DU).

A vertical column of air extending from the earth's surface to the top of the atmosphere, when reduced to standard temperature and pressure (STP), contains the number of molecules per cm^3 equivalent to Loschmidt's

number = 2.69×10^{19} . This column contains a total of 8×10^{18} ozone molecules cm^{-2} (the global average total amount of ozone per cm^2 above sea level) occupying a thickness of approximately 0.3 cm (STP) or 300 milli-atmosphere cm, defined as 300 Dobson units (1 DU = 10^{-3} cm of ozone). This vertical column measurement is known as a total ozone measurement. In comparison, under the same temperature and pressure conditions, the original vertical column of air would be over eight kilometers high (Dotto and Schiff, 1979). This puts in perspective ozone's contribution to the atmospheric composition.

Total ozone measurements are made from ground-based instruments or satellite-borne instruments. The standard ground instrument is the Dobson spectrophotometer. This instrument is a double monochromater which measures the differential absorption of the solar irradiance at two adjacent wavelengths. A standard set of paired wavelengths, distinguished as A, B, C, C' and D, has been incorporated in the measuring technique. Since one wavelength of the pair absorbs ozone more strongly than the other, total ozone can be determined by the ratio of the irradiances measured at each wavelength. Although measurements made on zenith blue skies are most accurate, measurements on cloudy days or even in the moonlight are considered accurate enough to be useful. The Dobson spectrophotometer is thought to be accurate to within 2-3

percent (London,1984). The instrument is currently out of production and is being replaced by the Brewer spectrophotometer which yields comparable results (WMO,1985).

The M-83 filter instrument is used in the Soviet Union and in Eastern Europe for total ozone measurements. This instrument also determines total ozone by the differential absorption of the solar irradiance at two different wavelengths. In direct comparison measurements, Bojkov (1969) found differences by as large as 40 percent between the Dobson spectrophotometer and the M-83. These differences are based on the quality and calibration of the optical filters and the measured ozone absorption coefficients assumed to be constant throughout the atmosphere used in the reduction of the data. However, the overall accuracy of the M83 is considered to be within 3-5 percent (London,1984).

Satellites have greatly enhanced the measurement of total ozone with the employment of two techniques. One technique analyzes the solar UV radiation backscattered from the earth and atmosphere, whereas, infrared emission at 9.6 μ m from both the ground and the atmosphere is monitored in the second technique.

In the backscattered ultraviolet (BUV) method, the outgoing radiation that has first been absorbed by ozone along the path of the solar beam and then scattered back

to the satellite by the earth and the atmosphere is measured (Klenk, 1982). Obtaining total ozone amounts is possible because of the separation of the absorber (ozone) from the scatterers (the surface and the troposphere). The reflecting surface and almost 90 percent of the scattering atmosphere lie below the tropopause above which 80 - 90 percent of the ozone lies. Therefore, in the wavelength range of interest, ozone essentially acts as the only attenuator of the direct solar flux and the diffuse reflected and scattered radiation. Total ozone can then be reasonably approximated by a method similar to the Dobson technique. A shortcoming of the BUV technique is that the satellite instrument is less sensitive to changes in ozone in the lower troposphere than the ground-based system. Also, no measurements are available in regions of polar dark. Aboard the satellite Nimbus-7 is the Solar Backscatter Ultraviolet (SBUV) instrument which is an improved version of the Backscatter Ultraviolet (BUV) experiment that flew on the Nimbus-4 satellite measuring total ozone from early 1970 to December 1977. The SBUV is a nadir viewing double monochromator designed to measure total ozone and also the vertical distribution of ozone (Heath et al., 1978).

The Nimbus-7 satellite also provides the platform for the Total Ozone Mapping Spectrophotometer (TOMS). The TOMS is designed to provide daily global coverage of the

earth's total ozone. Both the SBUV and TOMS measure total ozone in a similar manner using nearly identical wavelengths. However, the TOMS yields much finer resolution. From a nearly polar, sun-synchronous orbit, TOMS scans in a plane perpendicular to the orbital path to produce daily global ozone measurements of between 50 and 100 km resolution (Heath et al., 1978). SBUV's resolution is about 200 km in the nadir direction only.

Ozone absorbs strongly in the infrared (IR) at $9.6\text{ }\mu\text{m}$ and measurements of upward-directed infrared radiation at this wavelength by satellites can estimate the total ozone in a vertical column. The Limb Infrared Monitor of the Stratosphere (LIMS) also aboard Nimbus-7 operated from October 1978 to May 1979. Remsberg et al. (1984) reported that column ozone measurements from 0.1 mb to 70 mb calculated using LIMS data are very accurate. Because the limb viewing geometry causes high opacity at lower altitudes, ozone measurements below 70 mb, however, may be in error by as much as 20 percent. Therefore, satellite IR measurements to determine total ozone are not as accurate as the other methods, but as discussed in the next chapter, IR techniques are used to measure ozone's vertical profile.

Total ozone measurements derived from ground-based instruments and satellite-borne instruments may not be similar for a variety of reasons. Initial differences may

arise from the ozone absorption coefficients used in the algorithms since the two systems use different sets of wavelengths. There are also calibration differences between different ground stations and between the ground stations and satellite systems. Also important are the spatial differences. Satellite observations are almost completely global whereas there is a great spatial inhomogeneity of the ground based system, especially in the Southern Hemisphere (London, 1984). The SBUV and TOMS total ozone measurements are about 8 and 6 percent lower, respectively, when compared to ground-based measurements (Bhartia et al., 1984).

3.2 Ozone Transport and its Global Distribution

Maximum local concentrations of ozone are observed in the lower stratosphere and the maximum values of total ozone are observed at polar latitudes in late winter and early spring. As previously mentioned, ozone is formed in the middle and upper stratosphere with maximum production over the equatorial regions. The fact that the bulk of the ozone is well away from its source region clearly suggests that ozone undergoes transport to higher latitudes.

The strong latitudinal differences are depicted in Fig. 3 which shows the global long-term average of total ozone obtained from the BUV instrument on the Nimbus-4

satellite from 1970 to 1977. Within the stratosphere, the overall mean mass flow is directed poleward and is downward outside the tropics. This flow accounts for the transport of ozone from the region of maximum production in the equatorial middle stratosphere to the region of maximum concentrations in the lower stratosphere of the polar regions (Fig. 4). The seasonal variations of total ozone are depicted in Fig. 5. High total ozone values in the high latitudes of the winter hemisphere are accounted for by the strong poleward and downward mass flow at that season. The mass flow shown in Fig. 4 should not be confused with the eulerian mean meridional circulation which at high latitudes in winter is directed upward and equatorward (Holton, 1979). This apparent paradox may be resolved by recalling that planetary waves are very active in the winter stratosphere and that these waves produce eddy fluxes which contribute to the transport of ozone. Thus, it is now generally believed that the seasonal variation of ozone, as shown in Fig. 5, is driven by a Langragian circulation and the interaction between large-scale planetary waves and the circumpolar vortex (Rood, 1983).

The winter polar stratospheric circulation is characterized by strong westerly winds creating a circumpolar vortex. This vortex essentially prohibits any transport of ozone from lower latitudes to the pole during

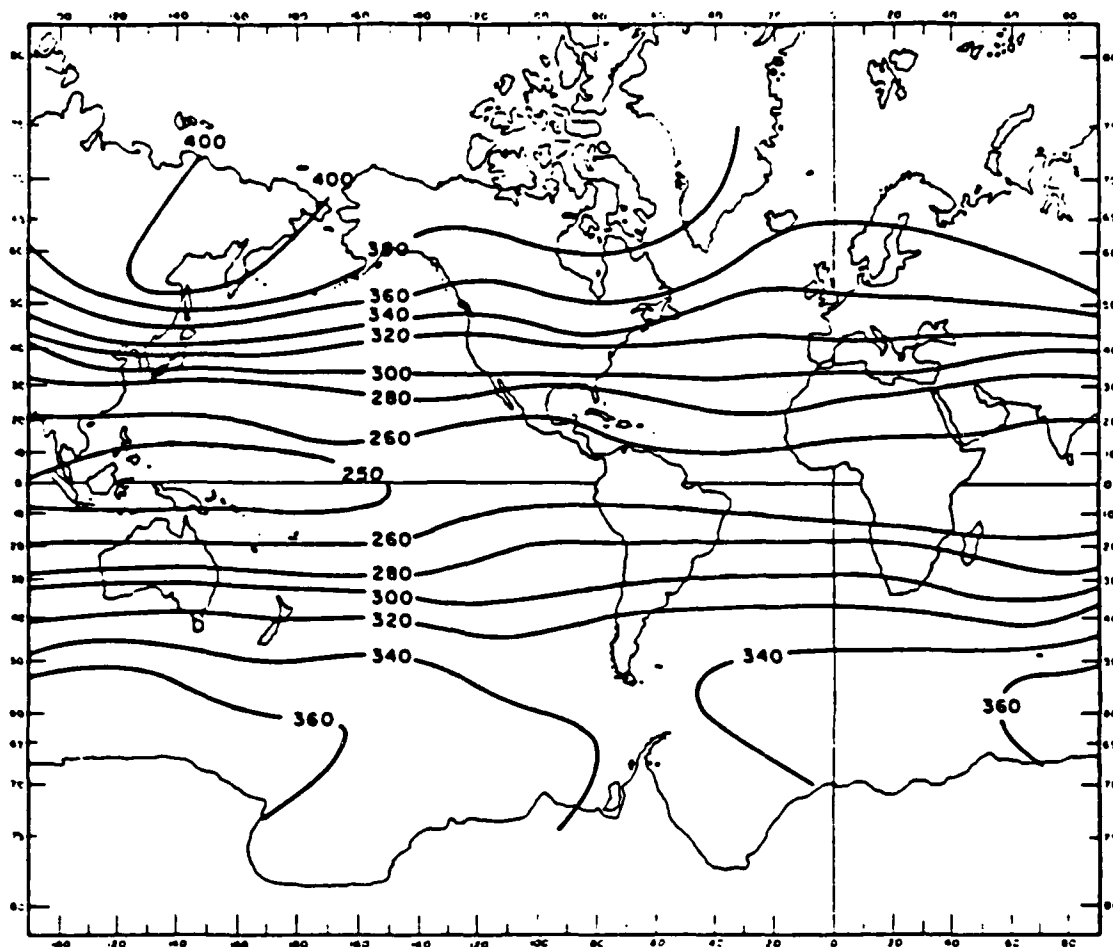


FIGURE 3. The global long-term annual average of total ozone in Dobson units observed during the period April 1970 to March 1977 as measured by the BUUV instrument on Nimbus-4.

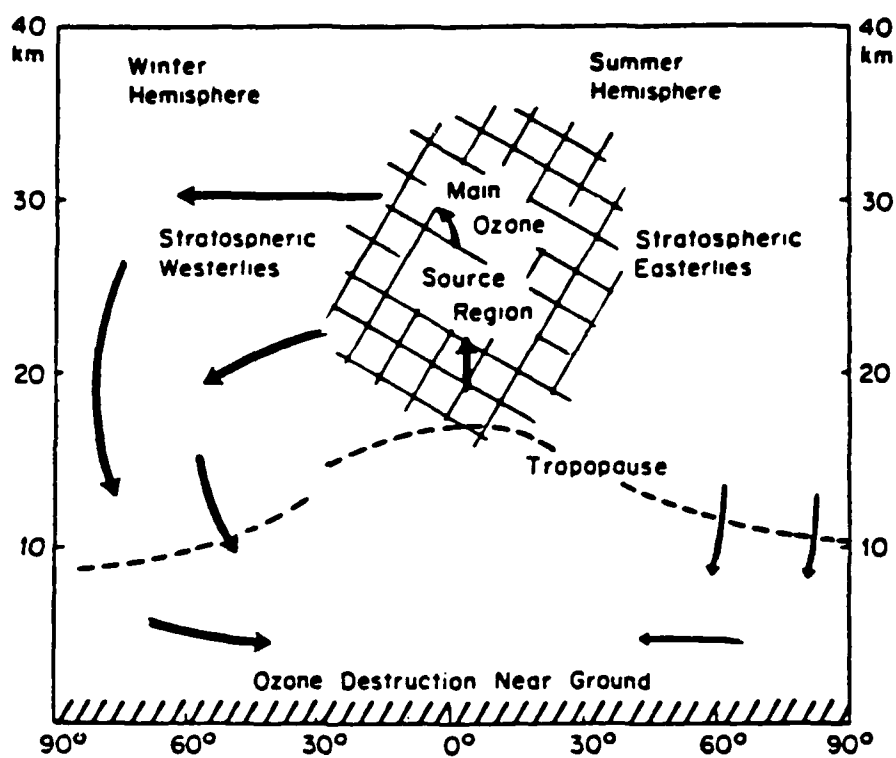


FIGURE 4. A schematic illustration showing sources, sinks and mass transport of ozone. (Dutsch, 1971).

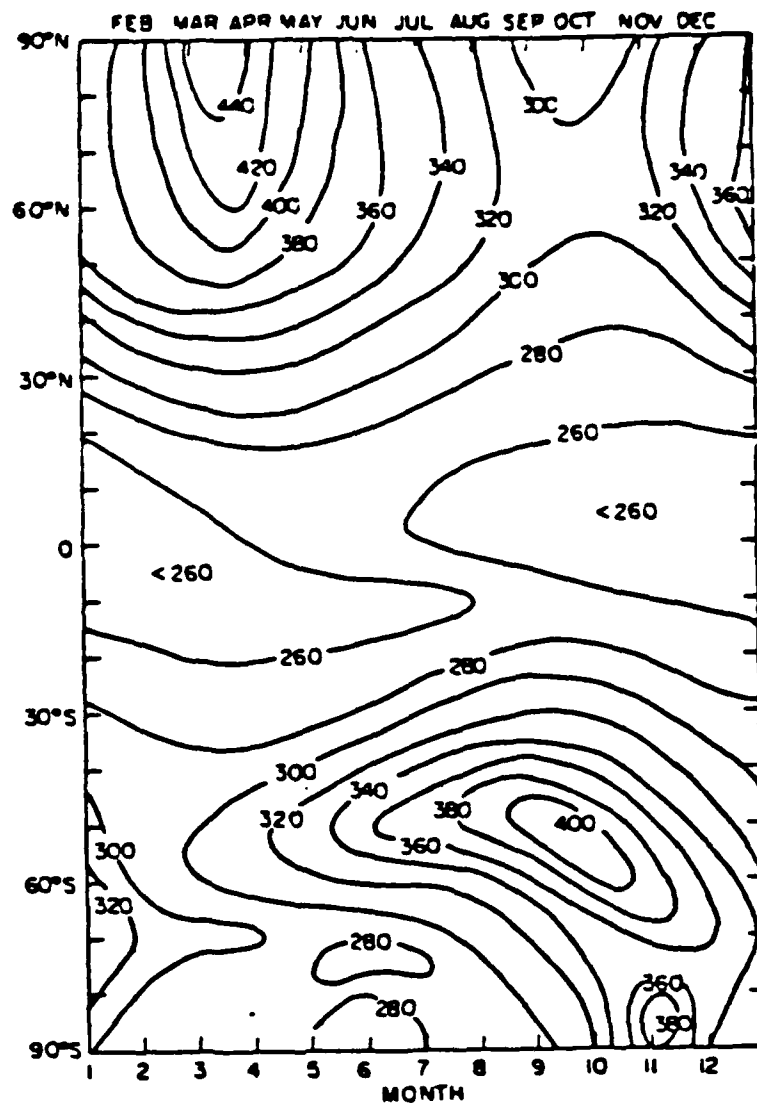


FIGURE 5. The seasonal columnar variation of total ozone in Dobson units as a function of latitude (Dutsch, 1971).

the winter months. However, planetary waves work to decelerate these zonal winds and weaken the vortex by transporting heat, momentum and among other things, ozone, into the polar regions. This breaking down of the vortex and transport of heat into the polar region is known as a stratospheric warming. A stratospheric warming is defined as minor if a significant temperature increase is observed (i.e. at least 25 K in a period of a week) and the criteria of a major warming is not met. A major warming is a reversal of the temperature gradient at 10 mb from 60 degrees latitude to the pole and easterlies are observed (NASA, 1978).

Since the Northern Hemisphere has more intense planetary wave activity due to its land-sea contrast, the Arctic stratosphere experiences several major and minor mid-winter stratospheric warmings. As a result, the meridional ozone transport is greater and the mean annual high latitude maximum is larger than that in the Southern Hemisphere. On the other hand, the much stronger westerlies (deeper vortex) in the Antarctic vortex account for the delay of any major or minor warming event to much later in the spring. Interest in the polar stratospheric circulation and stratospheric warmings has recently increased in the advent of the Antarctic ozone hole problem which is discussed in chapter VI.

Ozone is inversely correlated to pressure patterns in the upper troposphere and lower stratosphere (Gotz,1951;Craig,1965). Within a well-developed upper level trough at the 50-100 mb region, air parcels flowing northwesterly, downstream from ridge to trough, undergo subsidence and vertical convergence which increase local ozone concentrations. A horizontal advective effect also prevails since the air parcels originate in an area of greater ozone content. Similarly, there is also a longitudinal variation in total ozone which is mostly associated with quasi-stationary planetary waves. This variation would be more pronounced in winter and spring when the troughs are deeper.

In the tropical stratosphere, there is a near 2-year (quasi-biennial) oscillation of the zonal wind. Associated with this is a weak, but detectable oscillation of total ozone and local ozone concentration in the lower and middle stratosphere (Oltman,1982). Observations reveal that increased ozone amounts are in phase with increases in the westerlies in the tropics while lagging with respect to the westerlies in the higher latitudes.

Chemistry also plays an important part in the seasonal maximum as a result of the cold polar stratospheric temperatures slowing down the ozone depletion rates and the low solar angle reducing photodissociation rates. Thus, the relaxation times of

ozone are relatively longer during the late winter and early spring months (Cunnold et al., 1980).

CHAPTER IV

THE VERTICAL DISTRIBUTION OF OZONE

4.3 Measurements of the Vertical Distribution of Ozone

There are several ways to measure the vertical distribution of ozone based on direct (in-situ) or indirect (remote) observing techniques. Remote systems employ either the ground-based spectrophotometer or satellite platforms while the in-situ measurements are made by rocket, balloon or aircraft-borne instruments.

The standard ground-based method for determining the vertical profile of ozone is the Umkehr technique (Mateer, 1965). Here the spectrophotometer is used to measure the mean ozone concentration in nine standard layers of the atmosphere to an altitude of about 48 km. Measurement of scattered zenith light at two different wavelengths are made while the solar zenith angle is between 60 and 90 degrees. The ratio of the two measured intensities shows a steady decrease with increasing angle of the sun and then increases just before the sun sets. Hence, the term Umkehr which means turning back or reversal. The vertical ozone distribution is determined by making adjustments to the ozone amounts in the nine standard layers as obtained from a standard profile until the calculated and the observed Umkehr curves match sufficiently well, especially near the reversal point.

A new method for obtaining ozone profiles known as the "short Umkehr" method has been tested and accepted recently. The short Umkehr method makes use of zenith sky measurements in the more restricted range of solar zenith angles between 80 and 89 degrees. The shorter method consumes less time and appears to be as efficient as the conventional method (WMO,1985).

Remote sensing of ozone by satellite are of three types, two of which are on the Nimbus-7 satellite. The SBUV is based on the Umkehr technique and measures the backscattered UV radiation from different levels in the atmosphere. The second method is a limb-scattering technique observing atmospheric IR or visible light emission in the different layers. This method was demonstrated by the Limb Infrared Monitor of the Stratosphere (LIMS) which operated nearly flawlessly from October 25,1974 to May 28,1979, its expected lifetime (Remsberg et al.,1984). Finally, the Stratospheric Aerosol and Gas Experiment (SAGE) measures the absorption in the UV or visible ozone absorption bands as solar radiation is occulted by the earth's atmosphere (Kent and McCormick,1984). SAGE was launched on February 18, 1979 on a dedicated spacecraft and operated until November 1981. The non-sun-synchronous orbit of the spacecraft limited the coverage of SAGE to specific latitudes compared to the other two instruments.

Other methods to determine ozone's vertical distribution are in the developmental stage using IR, microwave and LIDAR techniques. In fact, a current LIDAR system can measure the ozone distribution to within 3 percent at altitudes of 30 to 50 km, an important layer for early detection of ozone depletion (Pelon et al., 1982).

For determinations of vertical ozone profiles with good vertical resolution, direct soundings are required. In-situ measurements of ozone in the free atmosphere have been made with instrument-laden balloons, rockets and airplanes. These instruments may use chemical or optical methods to measure ozone (Regener, 1960; London, 1984). While aircraft have definite altitude limitations, balloonsondes and rocketsondes can reach up to 40 and 70 km, respectively.

4.2 Vertical Ozone Profile

Figure 6 shows the long term average vertical ozone distribution at Resolute, Canada and Wallops Island, Va. The abscissa shows the partial pressure of ozone and the ordinate shows the atmospheric pressure and approximate height. The tropospheric level of ozone remains relatively constant with height. This is a result of strong vertical mixing due to turbulence. As we continue into the lower stratosphere, the ozone partial pressure

increases with height. At Resolute, which is the more northern station, the higher partial pressure, around 175 nb, is reached at an altitude of 20 km, whereas at Wallops Island a lower maximum ozone partial pressure of 150 nb is found at an altitude of approximately 24 km. This height of the maximum in the ozone partial pressure varies with season and latitude.

The vertical profile may show a well-defined maximum, a broad flat maximum or, on occasion, one or more secondary maxima. In general, the lower the height of the stratospheric maximum, the greater the concentration of ozone at that level. Again, this is a result of poleward and downward transport from the tropical middle and upper stratosphere where most of the ozone is produced. Fig. 6 shows that, at higher altitudes, the ozone concentration is greater at Wallops Island, the more southerly station. This is due to photochemical effects. More ozone is produced at this level at the southern station with higher photochemical equilibrium values than at the northern station.

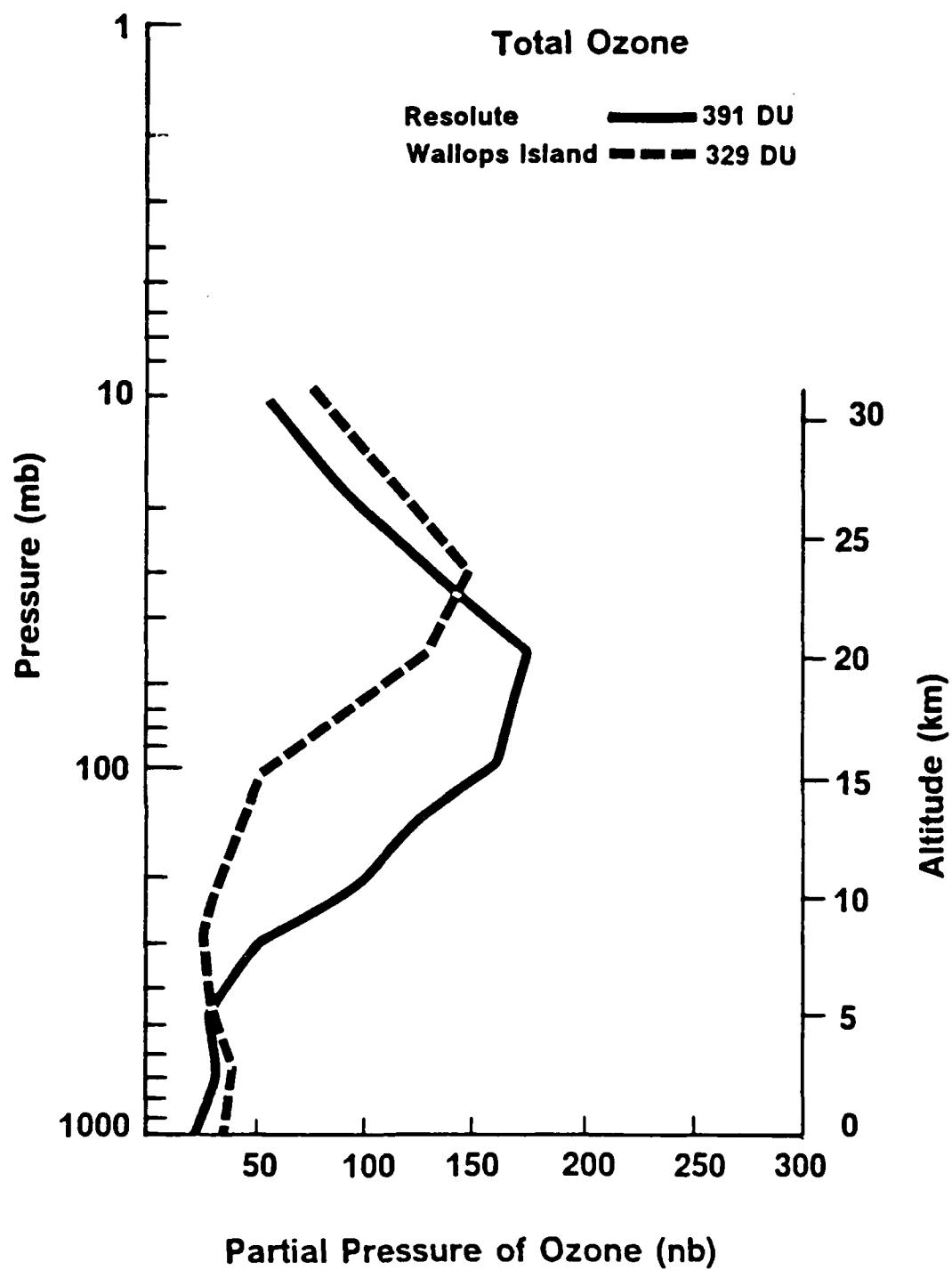


FIGURE 6. Mean long-term vertical ozone profile at Resolute (75 N) and Wallops Island (38 N).

4.3 Tropospheric Ozone

A large amount of ozone is transported into the troposphere each year by intrusions of stratospheric air through the tropopause. There exists a large positive correlation between ozone mixing ratio and potential vorticity deviations in the lower stratosphere and upper troposphere (Hering, 1965). Using large scale analysis of potential vorticity, Danielson (1968) used the term "folded tropopause" for the intrusion of the stratosphere into the troposphere. Such folds occur in conjunction with upper level frontogenesis and are major source mechanism of tropospheric ozone.

The folds develop by a steepening of the tropopause at the jet core followed by a downward and southward stretching of the jet (Fig.7). The descending air on the north side of the jet is stratospheric in origin and rich in ozone. The air on the south side is tropospheric. The atmosphere adjusts to this rapid downward and southward transport of horizontal momentum by forcing warmer air downward on the southside and cold air upward on the northside of the jet (WMO, 1985). This leads to a thermally indirect circulation which folds the tropopause and irreversible transport of ozone from the stratosphere to troposphere.

The tropospheric contribution to the total ozone is relatively small (~10%) but is very important in urban

areas. Ozone is the major oxidant in smog and the amount formed in the lower troposphere has a complex dependence on time of day, meteorological conditions, and the amount of pollutants in the air.

In the morning, ozone concentrations are very low. Since nitric oxide is a by-product of combustion, early morning rush hour traffic results in a rapid increase of nitric oxide. In the ambient air, NO is converted to NO₂. As depicted in fig. 8, the photodissociation of NO₂ by sunlight forms equal numbers of nitric oxide molecules and oxygen atoms. The ozone reacts with nitric oxide on a 1:1 basis, to reform nitrogen dioxide. Only a small steady state concentration of ozone results from this cycle. When combustion by-products in the form of hydrocarbons are present, they form peroxy radicals that oxidize the nitric oxide directly into nitrogen dioxide. This leaves very little of the nitric oxide to react with the ozone, so the ozone concentrations build up.

The concentration of ozone in the polluted atmosphere is controlled by the intensity of the sunlight and the ratio of NO₂ to NO. Once the sun sets, ozone is lost by reactions with various trace species in the atmosphere and concentrations go down.

While the geographical, seasonal, and day-to-day variations are mostly due to transport, there are many diverse physical and chemical factors which have a

pronounced influence on ozone. Some are natural, others are not.

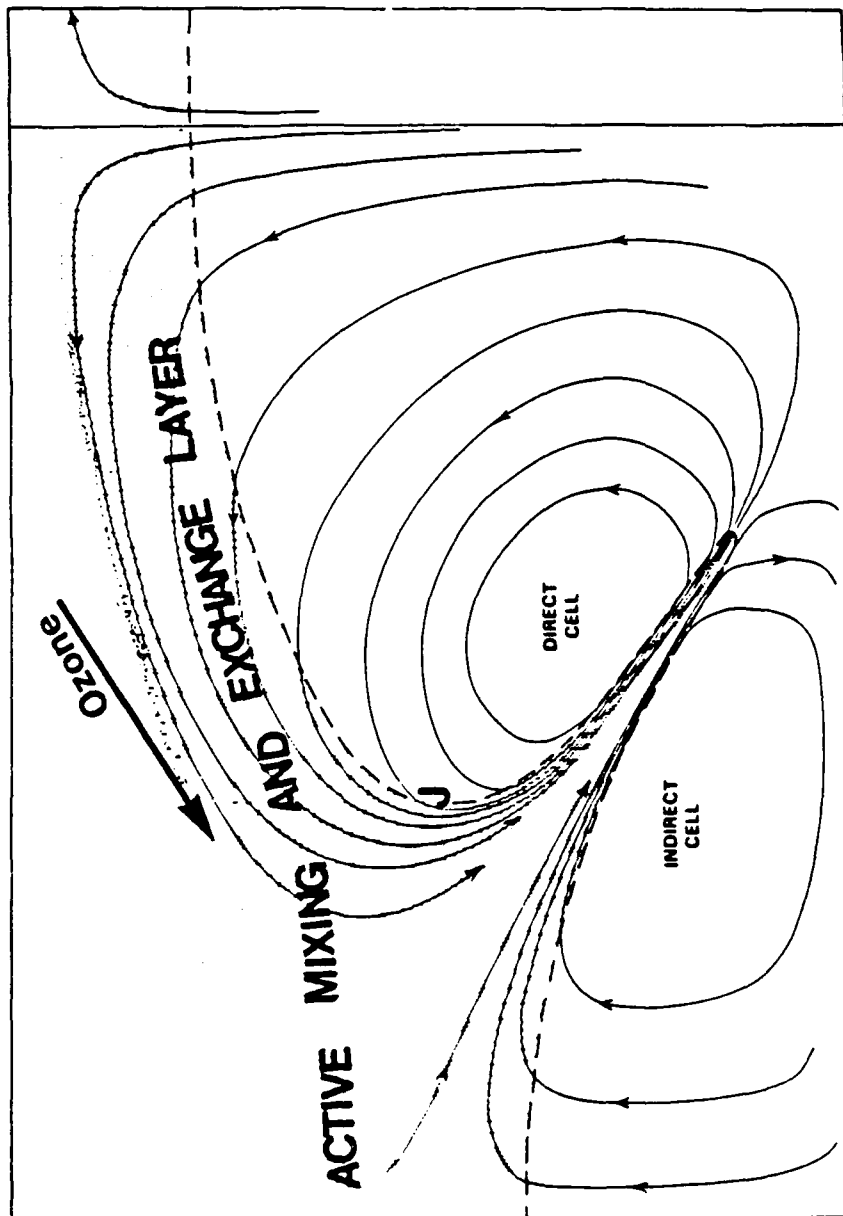


FIGURE 7. Stratospheric-tropospheric exchange process known as tropopause folding is illustrated. Measurements of atmospheric tracers such as ozone or potential vorticity can be used to identify air of stratospheric origin (after Danielson, 1968).

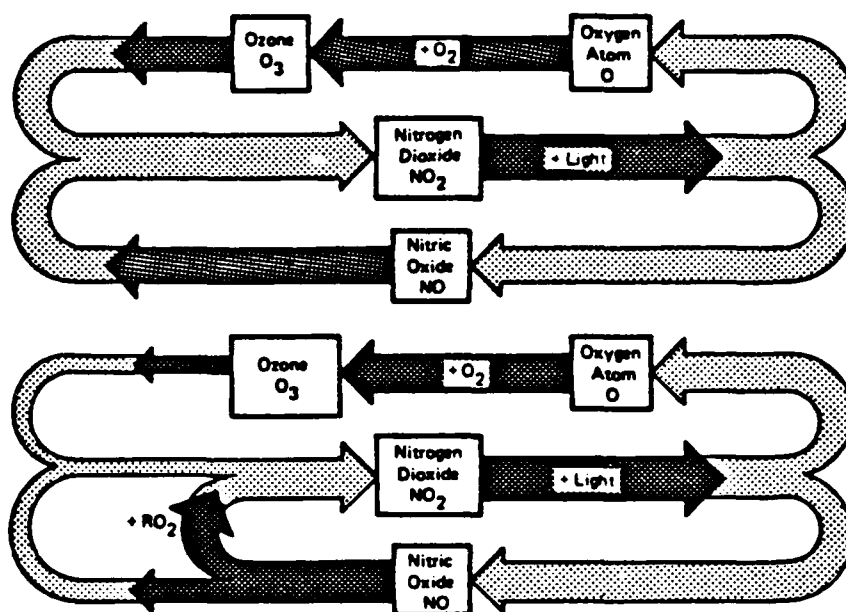


FIGURE 8. The NO-NO₂-O₃ cycle in air contaminated with NOx only (above) and with NOx and hydrocarbons (below).

CHAPTER V

PERTURBATIONS OF THE OZONE LAYER

5.1 Natural Perturbations

Since the generation of an oxygen containing atmosphere, a delicate chemical balance had maintained ozone levels in an approximate steady state with only relatively small natural variations. The ultimate source of stratospheric ozone is the sun. Any factor disturbing the solar UV output has an impact on the ozone layer by changing the temperature, photochemistry, and dynamics of the stratosphere from the resulting change in heating.

Investigators have observed a decrease in ozone with decreased solar UV fluxes due to the solar 11-year cycle of sunspot activity and the 27-day solar rotation. An analysis of seven years of Nimbus 4 BUV data by Chandra (1983) has shown that the globally averaged ozone in the upper stratosphere decreased by 3 to 4 percent from 1970 (solar maximum) to 1976 (solar minimum). Others have suggested changes of up to 8 percent in the layer between 32 and 48 km due to the change in solar activity (Penner and Chang, 1978; Gille et al., 1984), with negligible effects below 30 km.

Solar Proton Events (SPE) are an influx of high energy protons released by the sun and channeled by the geomagnetic field into the polar region. The incoming

particles collide with and ionize atmospheric molecules producing oxides of nitrogen (NOx) and hydroxyl radicals (OHx) which destroy ozone. The effects of several SPEs have been studied (Heath et al., 1977; Solomon et al., 1981; Thomas et al., 1983; Weeks et al., 1972) and ozone depletions from 30 to 70 percent have been observed at altitudes from 50 to 70 km. Both short term (1 day or less) and long term (1 week or more) ozone responses have been observed. These responses are understood to result from HOx (shortlived) and NOx (longlived) related chemistry (WMO, 1985). Changes above the stratopause are expected to be that due to HOx radicals, while NOx production effects become important mostly below that level.

Other cosmic events may also generate NOx and HOx in the upper reaches of the atmosphere. Thorne (1977) suggests important ozone perturbations can occur when high energy electrons from the earth's outer radiation belts produce NOx when they bombard molecular nitrogen in the mesosphere and upper stratosphere during geomagnetic storms. In these cases, however, the bulk of the ozone lies below the depletion region, thus there is very little effect (<2%) on the total ozone column by these extraterrestrial events (Turco, 1984).

There are other extraterrestrial events which may have a greater influence on the ozone layer. Turco et al.

(1981) studied the Tunguska meteor fall of 1908 and estimated that for several months local ozone depletions of up to 85 percent above 10 km within ten degrees of latitude from the impact area due to the generation of NO_x when the meteor entered the atmosphere. Some researchers (Clark et al., 1977) believe that the most catastrophic cosmic event responsible for ozone depletions could be a supernova occurring within 100 light years of earth. The resulting shower of intense UV, gamma and cosmic rays might well destroy 80 percent of the ozone layer. Reid et al. (1976) believe this to be a possible mechanism for previous mass extinctions of terrestrial and marine animals.

Events such as volcanic eruptions, natural gas emissions and even the hydrologic cycle can upset the ozone balance. Large injections of gases and dense volcanic particles effect ozone chemically and can alter photodissociation rates and stratospheric temperatures. Water vapor has a role in the thermal balance of the stratosphere which, if altered, can effect ozone amounts. Also, water vapor and natural gas emissions can eventually be transported into the stratosphere, broken down photochemically and then react with ozone. Warming of the stratosphere due to the absorption of heat by aerosol particles changes stratospheric dynamics. After the volcanic eruption of El Chichon in March-April 1982, an

ozone decrease on the order of 10 percent was observed between 100 and 30 mb (Dutsch,1985). Vupputuri (1985a,b) estimated roughly a two percent decrease depending on latitude and season as a result of ozone photochemistry interacting with the El Chichon stratospheric aerosol cloud.

A major El Niño event which was associated with extraordinary climatic anomalies took place in 1982 and 1983. A series of wintertime stratospheric warmings with possible ozone perturbations also took place at this time. However, Quiroz (1983a,b) found difficulty in separating any stratospheric temperature change from the El Chichon event from that due to El Niño to determine the effect on ozone.

5.2 The Catalytic Cycle

There are many processes responsible for the perturbations of ozone in the stratosphere. Ozone can be transported into the troposphere by tropopause folding where, in addition to photolysis, it can eventually react with one of the layer's gas constituents or the earth's surface. This process is relatively slow and accounts for about a percent of the ozone loss (NRC,1983). Another method is the removal by the classical reaction:



Again, this process is slow due to the cold stratospheric temperatures and is responsible for a fraction (<1%) of the ozone destroyed. By far, the most efficient and dominant process of ozone reduction is by catalytic reaction.

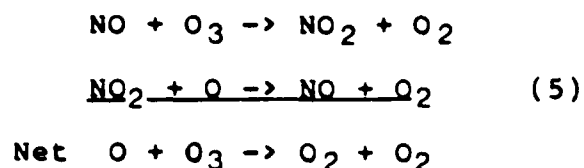
A substance is a catalyst if it serves to drive or enhance a process or reaction without being consumed in the process. Chemical catalysis can be an extremely efficient process and can occur naturally, as in the case of SPEs producing NO_x which catalytically attacks ozone. However, it was the realization that certain atmospheric pollutants could generate catalysts to destroy the ozone layer that caused the ozone controversy of the mid-Seventies.

5.3 Anthropogenic Influences

In the last fifteen years, it has been recognized that human activities can have a pronounced effect on the ozone balance. The first concern of man's influence on the ozone layer related to the effects of nitrogen oxides (NO_x) and H₂O generated in the stratosphere by supersonic transport aircraft (SST) exhaust (Johnston, 1971; Crutzen, 1971).

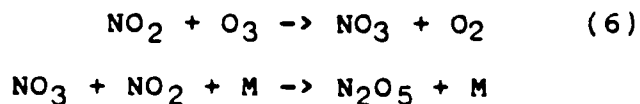
The nitrogen oxides NO and NO₂, taken together are generally referred to as NO_x, while the total odd nitrogen family (NO + NO₂ + NO₃ + N₂O₅ + ClONO₂ + HNO₄ + HNO₃) that

interchange photochemically with one another on a relatively short time scale (weeks) are known as NO_x. The oxides of nitrogen (NO_x) react with ozone by the catalytic cycle:

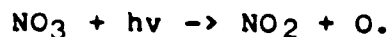
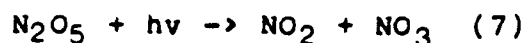


This cycle repeats itself over and over again and one molecule of NO_x can destroy many molecules of ozone. Between 25 and 45 km, these reactions dominate processes controlling the ozone balance in the contemporary stratosphere, contributing to most (45 - 60%) of the natural ozone chemical loss mechanism (WMO, 1985; NRC, 1983; Johnston and Podolske, 1981; Turco, 1978).

Studies of the odd nitrogen family must also include the longer lived reservoir species (N₂O₅, ClONO₂, HNO₄, HNO₃) which play a role in the variability of NO_x because of their unique chemical properties. For example, the production of N₂O₅ via the reaction:



occurs almost exclusively at night sequestering nearly 50 percent of the NO₂ at 10 mbar as N₂O₅ (WMO, 1985). Photolysis of N₂O₅ in the sunlit atmosphere is on a timescale of hours to days thru the reaction:



The product NO_3 is photolysed rapidly in the sunlit atmosphere yielding a second NO_2 molecule. Thus, the reservoir species of odd nitrogen in the atmosphere can control NO_x concentrations.

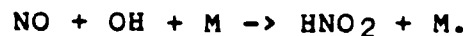
Injections of NO_x into the troposphere by subsonic jet aircraft can increase the column total of ozone. The subsiding NO_x reacts photochemically with rising hydrocarbons to produce ozone by a mechanism equivalent to that operating in the production of photochemical smog. The ozone thus formed tends to prevent the early detection by total ozone column measurement of any ozone depletion at higher altitudes.

Large nuclear explosions can deposit large quantities of NO_x into the stratosphere. Although analysis of the effects of such NO_x injections by the atmospheric nuclear tests of the 1950's and 1960's are inconclusive, it appears that the effect on the ozone layer was minimal (Bauer, 1979; Turco, 1978). A full scale nuclear war, however, may deposit up to 50 million metric tons (megatons) of NO in the upper atmosphere. The resulting depletion of ozone could be in the range of 70 percent. It is estimated that a five year recovery period would be required before the original ozone levels would be restored (Turco, 1984).

Besides its important role in the thermal balance of the stratosphere, water vapor also plays a role in the ozone balance. The HOx family consists of OH, HO₂ and H₂O₂ plus their major source gases H₂O and CH₄. The effects of HOx on ozone destruction are both direct and indirect. Water vapor is the dominant source of the hydroxyl radical (OH) through reaction with atomic oxygen. The direct effect is thought to dominate ozone destruction in the mesosphere and upper stratosphere through the reaction sequence (WMO,1985):



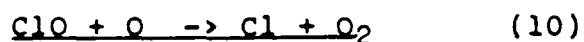
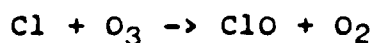
In addition, at lower altitudes the hydroxyl free radical, OH, can decrease NOx through the reaction:



Thus, OH may indirectly reduce the ozone loss by sequestering NOx in the lower stratosphere (Turco,1984).

While Johnston at the University of California, Berkeley is credited to alerting the scientific community to possible high ozone depletions due to SST exhaust emissions, two other University of California (UC) researchers are credited for starting the spray can controversy of the mid-Seventies. It has been over twelve years since Molina and Rowland (1974) of UC Irvine

published their classic paper pointing out the possible danger to stratospheric ozone by chlorofluoromethanes (also called fluorocarbons or chlorofluorocarbons). Chlorofluoromethanes or CFMs are an extremely inert family of man-made compounds used as spray can propellants (banned since 1978 in the USA, except for essential usage), refrigerants and foam blowing agents. In their paper, Rowland and Molina revealed that CFMs, while released at the surface, eventually diffuse upwards into the stratosphere where they photodissociate and catalytically attack ozone. CFMs absorb UV light at wavelengths short of 240 nm in the case of CFM-11, and 220 nm in the case of CFM-12 (Finlayson-Pitts and Pitts, 1986). At altitudes between 20 and 30 km, the light absorption releases a chlorine atom which catalytically destroy ozone via the cycle:



At first, these reactions were thought to be capable of depleting the ozone concentrations by up to 20 percent (Rowland and Molina, 1975). Now, under current chemistry, this process is thought to be the principle loss mechanism of ozone at levels of 30 - 50 km and capable of a 5 to 9 percent reduction in stratospheric ozone by the year 2000 (Prather et al., 1984).

A major temporary reservoir of chlorine in the middle stratosphere (25-35 km) is chlorine nitrate, ClONO_2 . It is formed at night by the recombination of ClO with NO and dissociates slowly in the daytime. Therefore, measurements of ClONO_2 are important for assessments of impacts on ozone since it may either sequester or release chlorine radicals as well as NO_x .

The proposed large fleet of SSTs and, therefore, the source of ozone destroying oxides of nitrogen never materialized for a variety of reasons, but this is not the case for CFMs. It is generally agreed that CFMs are the current major anthropogenic threat to the ozone layer. The production of some types of CFMs dropped after the spray can controversy of the mid-Seventies but, since 1982, a resurgence has been seen. Fig. 9 shows the estimated worldwide release rates of two of the most extensively used CFMs, CFM-11 and CFM-12.

One cause for concern with CFMs is their long atmospheric lifetimes of 40 to 150 years. The ozone depletion resulting from CFM release today may not become evident until well into the twenty-first century. A second concern is that as CFMs are strong absorbers in the infrared atmospheric window (8.3 μm - 12.5 μm), their increasing concentrations tend to exacerbate the greenhouse effect.

Other chemical agents such as bromine, methane, fluorine and carbon dioxide have direct or indirect effects on the ozone layer. Bromine species have the potential to destroy ozone more efficiently than the analogous chlorine compounds, but they are emitted mainly from natural sources (in particular the oceans) and anthropogenic contributions are small (<10%) (Bauer, 1979; Prather, 1984). Methane is oxidized in the stratosphere yielding HOx species which can influence the mixing ratio of ozone. Carbon dioxide increases can cause the stratosphere to cool and, as a result, slow the catalytic reaction rates offsetting the ozone loss (WMO, 1985). A summary of natural and anthropogenic perturbations of stratospheric ozone are presented in tables 2 and 3.

As new knowledge is gained, major changes have occurred in the predictions of ozone reduction resulting from man-made perturbations. The changes in ozone depletion predictions from CFMs at 1974 release rates and emissions of NOx by high-altitude aircraft are depicted in figure 10. Research has also revealed that interactions of simultaneous perturbations yield considerably different results from individual perturbations acting alone.

The earth's ozone layer responds to the various influences of many chemical and dynamical processes. Recent attempts to predict the effects on stratospheric

ozone have suggested only small perturbations (Bauer,1979; Prather et al,1984;Turco,1985). So far, the natural variability of the ozone layer has masked any changes in the total ozone. Or has it?

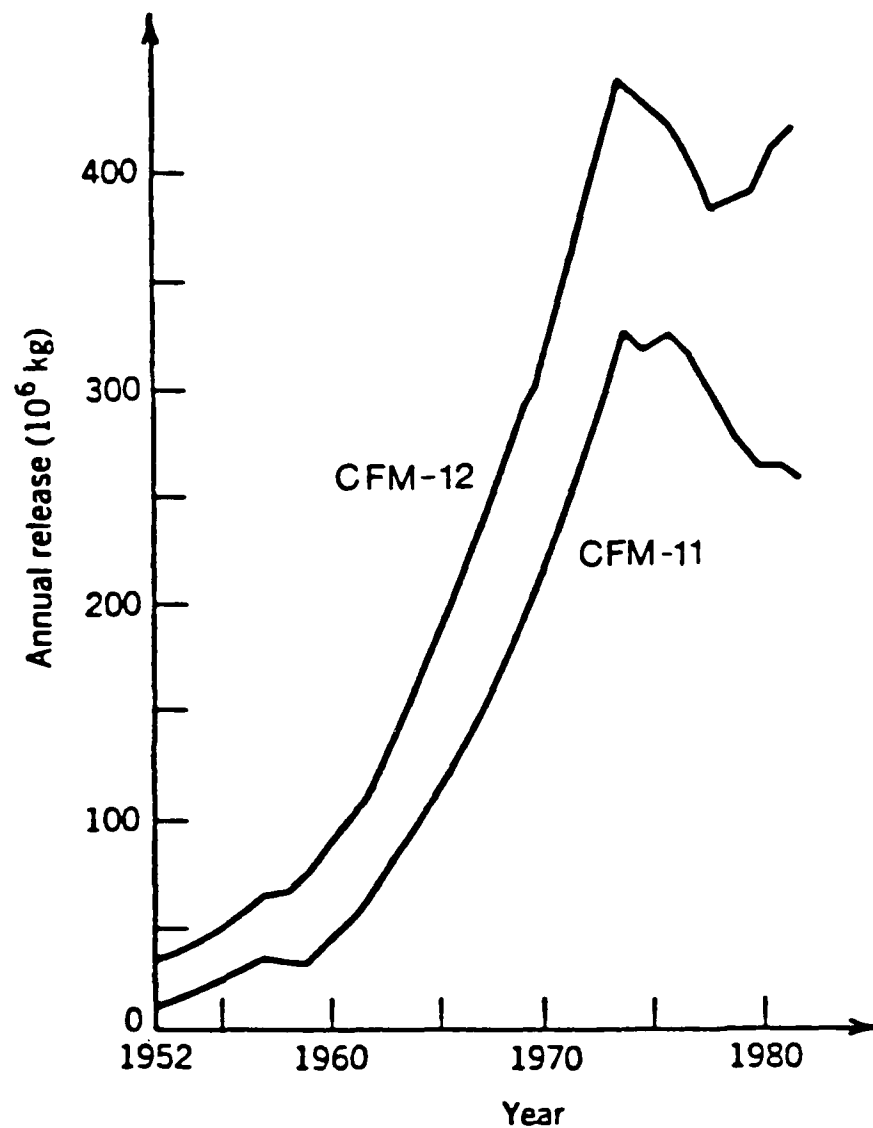


FIGURE 9. Estimated annual worldwide releases of CFM-11 and CFM-12 from 1952 to 1980 (NRC, 1983).

CALCULATED OZONE - COLUMN CHANGE TO STEADY STATE FOR TWO STANDARD ASSUMED PERTURBATIONS

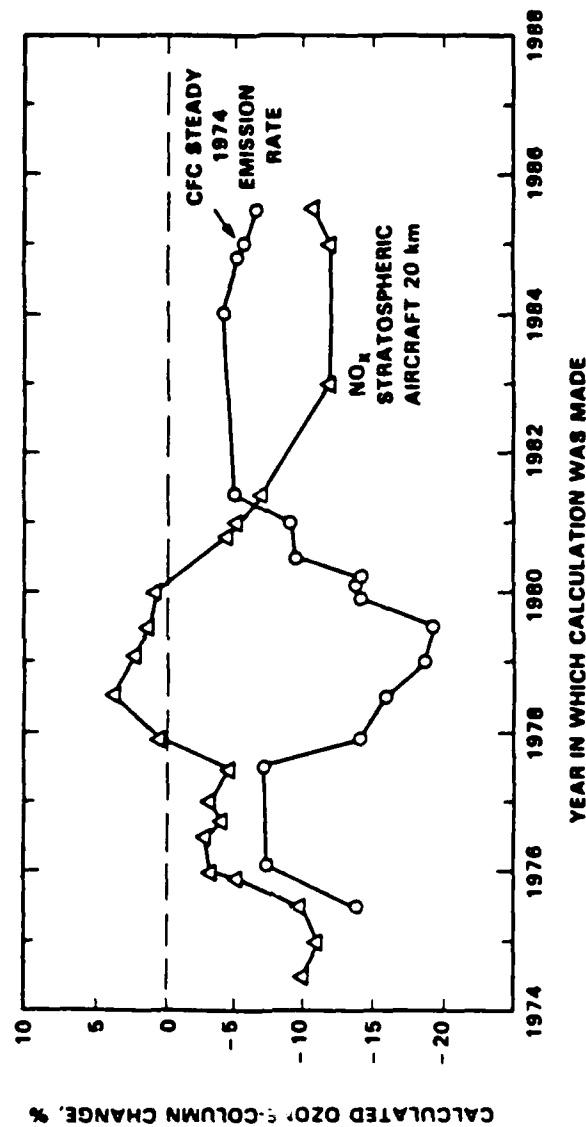


FIGURE 10. Historical trends in model predictions of steady-state ozone perturbations caused by a) 2000 molecules $\text{cm}^{-3} \text{ s}^{-1}$ of nitric oxide emitted over one kilometer interval centered at 20 km and b) CFM-11 and CFM-12 emitted continuously at 1974 rates (WMO, 1985).

TABLE 2
NATURAL EVENTS WHICH PERTURB
STRATOSPHERIC OZONE

EVENT	DESCRIPTION	EFFECT ON OZONE
Solar UV variations	Natural cyclic variations e.g. 11-year and 27-day	Ozone concentrations co-vary with UV flux at high altitudes but <1% change at stratopause (Eckman, 1986)
Solar eclipses	Short term interruption of sunlight	No appreciable effect (Vaughan, 1982)
Solar proton events (SPEs)	Protons emitted in solar storms penetrate the upper atmosphere producing NOx	A large SPE may cause a 20% at altitudes of 40 km. <2% effect on total ozone (Solomon et al., 1981)
Meteors	High velocity meteoric debris produces NOx in upper atmosphere	Rare large meteors may cause 10% depletion, but most meteors have little effect. (Turco et al., 1981)
Supernova	Energetic particles and radiation ionize atmosphere and produce NOx	If occurrence is within 100 light years the cosmic rays might cause 30-80% depletion for a hundred years (Clark et al., 1977)
Volcanoes	Emissions of gases and aerosols into the upper atmosphere	10% decrease of ozone observed between 100-30 mb due to El Chichon (Duttsch, 1985)

Unless otherwise stated, the effect is given as the percentage change in the average vertical ozone column concentration through the stratosphere for continuous pollutant emission at a fixed rate over a period exceeding the atmospheric transport and photochemical and equilibrium times.

TABLE 3
MAN-MADE CHEMICAL AGENTS WHICH
PERTURB STRATOSPHERIC OZONE

AGENT	SOURCE	EFFECT ON TOTAL OZONE
N ₂ O	By-product of combustion and denitrification of nitrate fertilizers	N ₂ O doubling leads to a 10 to 16% O ₃ depletion (WMO, 1985; Turco et al., 1978)
NO	Injection below 12 km by commercial aircraft	With present air traffic O ₃ could change from 0 to +2% (Turco, 1984)
	Injection by SST at 17 to 20 km	Ozone depletion could be 4 - 8% from a fleet of several hundred SST (Turco et al., 1978)
	Nuclear War	Ozone depletions of 30 to 40% are possible the first year after a 5000-megaton exchange (Turco, 1984)
CFMs	Industrial production	CFMs released at current rates could lead to ozone depletions of 2 to 8% in 50 to 100 years (Cicerone et al., 1983)
CO ₂	Biomass burning and fossil fuels combustion	Doubling of CO ₂ could increase ozone by 3 to 6% (WMO)

Unless otherwise stated, the effect is given as the percentage change in the average vertical ozone column concentration through the stratosphere for continuous pollutant emission at a fixed rate over a period exceeding the atmospheric transport and photochemical and equilibrium times.

CHAPTER VI

THE ANTARTIC OZONE HOLE

6.1 Formation of the Ozone Hole

Recently, Farman et al. (1985) reported on a remarkable depletion of total ozone measured at Halley Bay, Antarctica (76S 26W). Total ozone measurements have been taken at Halley Bay since 1957. However, the scientists noticed a steady decline in the mean October (Antartic spring) values. The measured ozone content was 30 percent lower in the springs of 1980 thru 1984 than in the springs of 1957 to 1973.

Earlier, Chubachi (1984) reported a decrease in total ozone with the largest reductions occurring at altitudes 14 to 24 km during September and October of 1982 at Syowa (69S 40E), the Japanese Antarctic Station. Analysis of TOMS data (Stolarski, 1986) confirmed these ground-based measurements. The region of minimum ozone covered the whole polar region extending out to about 60-70S, corresponding to the area enclosed by the southern stratospheric polar vortex. This apparent thinning in the ozone layer has been popularly named the "Ozone Hole".

The depletion occurs in September after the polar region is sunlit, with ozone decreasing at a rate of 0.6 percent per day (Stolarski et al., 1986), reaching a minimum value about mid-October. Fig 11 depicts mean

October total ozone values for Halley Bay from 1957 to 1984. Gardiner and Shanklin (1986) reported a mean October 1985 total ozone value of 192 DU, 2 DU lower than that of 1984. Fig. 12 shows October monthly mean TOMS total ozone maps for the Southern Hemisphere in each of the seven years from 1979 to 1985. The October monthly mean total ozone value, as measured by TOMs, declined from a about 260 DU in 1979 to 150 DU in 1985.

A similar, albeit smaller, ozone hole has since been observed in the Arctic. Here the minimum ozone content occurs in February and is equivalent to a decrease of about 2.6 percent per year (Weisburd, 1986). The depleted region is centered over Spitsbergen, Norway and is approximately one-third the areal extent of its Antarctic counterpart. Climatologically, this is the position and size of the Northern Hemisphere winter vortex, which is displaced off the pole by the Aleutian High.

The observed differences of the two regions of ozone depletion result largely from hemispherical differences in the thermal structure and dynamics of the winter stratospheres. In the northern hemisphere, large amplitude planetary scale waves induced by orographic features and land-sea contrast propagate upward into the winter stratosphere. This tropospheric forcing distorts the polar vortex and transports heat and momentum poleward. The heat partially compensates that lost by

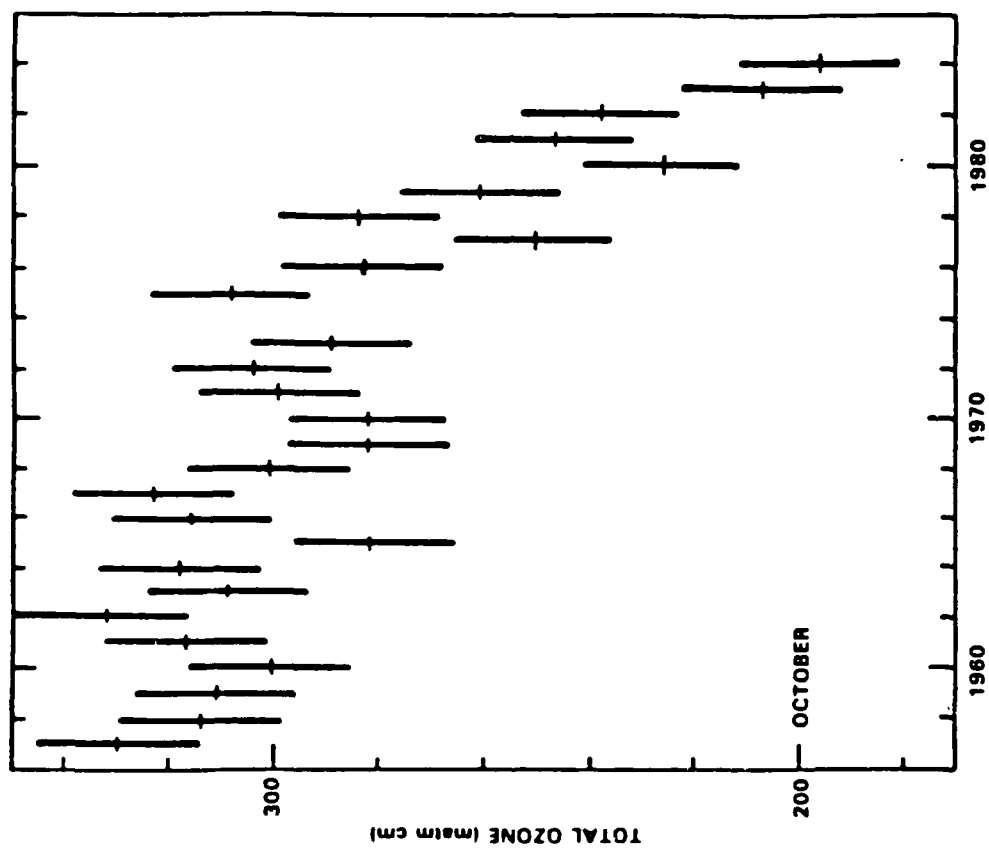


Figure 11 Monthly means of total ozone at Halley Bay for October of the years 1957 through 1984.

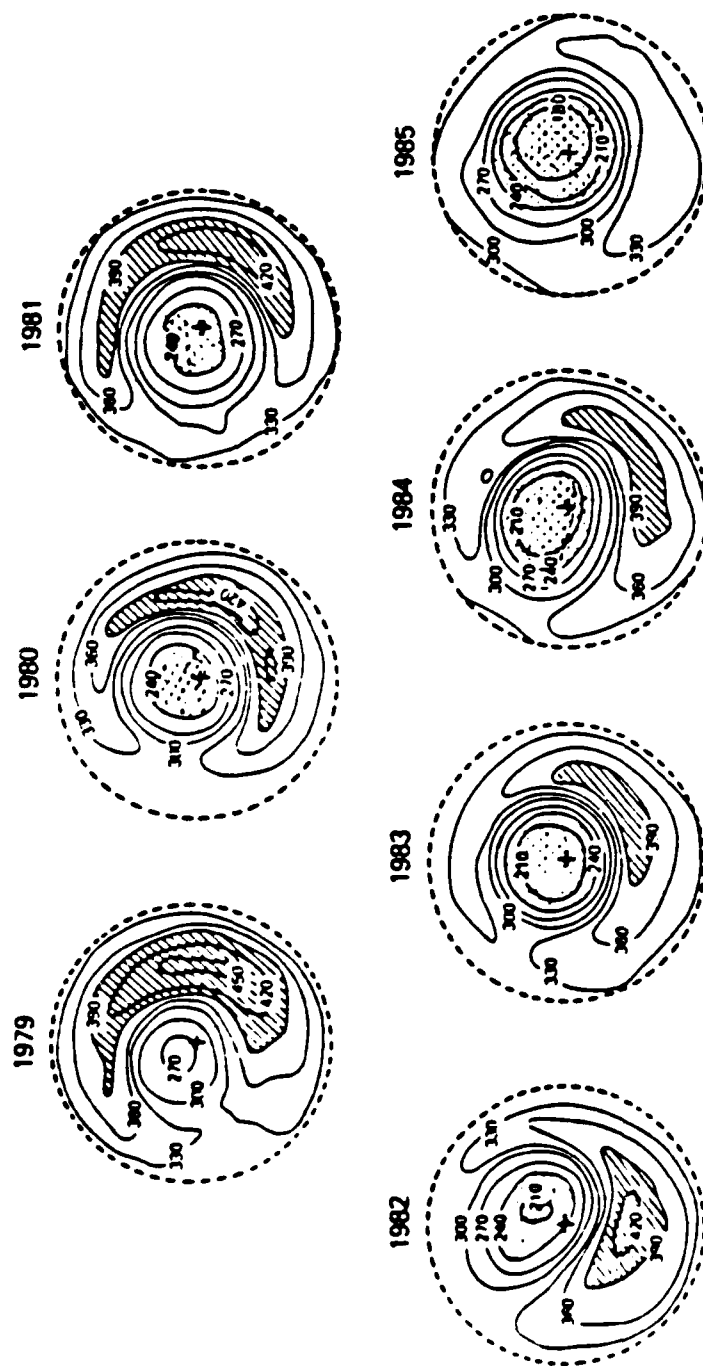


FIGURE 12. Six-year sequence of October monthly means of total ozone. The maps are south polar projections with the pole indicated by "+" and the 30° S latitude by a dashed circle. The Greenwich meridian is towards the top of each map. Contours are every 30 DU. The shaded regions indicate monthly mean total ozone amounts of <240 DU and >390 DU.

radiative cooling, allowing the vortex to remain relatively warm and less stable. In contrast, there is less tropospheric forcing in the Southern Hemisphere. The absence of large amplitude waves allow for a deeper, more stable and much colder vortex which maintains its integrity well into spring. The strength and timing of the vortex breakdown has a large effect on total ozone concentrations measured in the spring.

Low total ozone amounts at the poles in the spring have been observed since the late 1950's (Dobson, 1966; Wexler, 1960). This is a natural result of decreased production during the long polar night and a lack of transport from the equatorial source region. Stolarski et al. (1986) state that ozone values in the Antarctic before entering the polar night are very close to those values measured as the region leaves the polar night. It now appears that there are processes which cause the depletion of ozone after the start of the polar day (September). The identities of these important processes have been discussed by the various theories on the formation of the ozone hole.

6.2 Theories on the Formation of the Ozone Hole

Three basic theories of the formation of the ozone hole in the Antarctic region have so far been put forward. These three theories are:

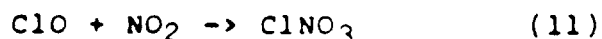
a) The ozone loss is caused by enhanced concentrations of odd chlorine and possible heterogenous chemistry associated with polar stratospheric clouds.

b) Rising air motions induced by radiative heating of aerosols within the polar vortex carries ozone-poor air from the troposphere to the stratosphere.

c) Extraterrestrial phenomena such as increased solar activity or meteors produce catalytic agents in the atmosphere which destroy the ozone and develop the hole.

Farman and his colleagues (1986) noted that the only difference between the present day atmosphere from that of previous decades is in the higher concentrations of chlorine. Their report suggested that the increasing levels of chlorine may be affecting ozone. Indeed, observations by Rasmussen and Khalil (1986) confirmed that concentrations of CFM-11 and CFM-12 at the South Pole have increased by a factor of two since 1975. Cronn et al. (1986) report annual rates of increase of CFM-11 and CFM-12 at Palmer Station, Antarctica of 5.87 and 5.45 percent, respectively, between 1982 and 1985.

In the lower stratosphere, chlorine is primarily contained within reservoir species such as ClNO_3 and HCL , the former produced through the reaction:



The British Antarctic Survey scientists suggested that during the long polar night, chemical interactions between NO_x and Cl_x , enhanced by the extreme cold of the polar winter, could cause a build-up of reservoir species that

would rapidly release chlorine at the onset of the polar day. The low solar angle in the polar spring results in attenuation of ultraviolet light at high latitudes. This restricts photochemical reactions for those molecules which absorb UV radiation (such as O_2) but still allows photolysis of Cl_2 at near UV and visible wavelengths. This process would provide a rapid source of ozone destroying chlorine provided levels of NO_x are low. Otherwise, reaction (11) producing $ClONO_2$ would result.

Solomon et al. (1986) support these ideas. However, they and others (Halakayama and Leu, 1986; Friedl et al., 1986) state that these reactions are too slow in the gas phase and occur above the bulk of the ozone layer (>25 km). Solomon et al. (1986) suggest heterogeneous reaction processes in the presence of polar stratospheric clouds. One reaction:



produces the chlorine free radical through the photolysis of Cl_2 . Another reaction is:



Both of these reactions tie up NO_x in the form of nitric acid (HNO_3). The production of $HOCl$ leads to HO_x radical formation as well as a chlorine free radical, so that the effect on ozone would be greater than that of chlorine alone. For these reactions to be effective, however, they

must take place on aerosol surfaces such as those provided by polar stratospheric clouds.

Polar stratospheric clouds (PSCs) are optically thin clouds which occur in the winter polar stratosphere and were first sighted by the Stratospheric Aerosol Measurement II (SAM II) instrument aboard Nimbus-7 (McCormick et al., 1982). Since then, PSCs have been observed by SAM II to be a regular feature in the winter of both polar regions whenever the ambient temperature falls below 195 K. In fact, McCormick et al. (1982) found an excellent correlation between the occurrence of PSC sightings and low stratospheric temperatures. PSCs were observed in more than 90 percent of the cases where the minimum temperature was 185 K or less, and at least 45 percent of the cases where the temperatures were 197 K or less. Since these kinds of low temperatures are more frequent in the Southern Hemisphere winter stratosphere, PSCs are more prevalent in the Antarctic than in the Arctic.

The SAM II system has observed PSCs in the Northern Hemisphere to occur at altitudes of about 20 km. The Antarctic PSCs occur at about 15 to 17 km, and possibly lower. McCormick and Trepte (1986), using SAM II satellite data, show that in the Antarctic stratosphere, PSCs slowly descend in altitude during the winter months. The data revealed possible transport down to 10 km in late September. The Antarctic stratosphere commences warming in

September and continues to do so more rapidly in October, during which time the clouds evaporate.

The composition of PSCs is still uncertain. Originally thought to be composed of water ice and small amounts of sulfuric acid (NASA, 1984), some investigators believe that the clouds are composed of supercooled droplets or ice crystals of nitric acid or hydrochloric acid (Toon et al., 1986; Hamill, 1986). The presence of PSCs at the altitudes and time of the ozone depletion suggest a more than casual relationship.

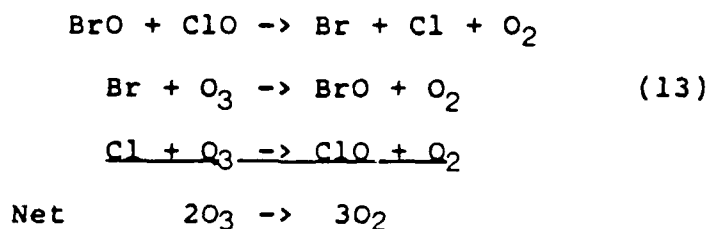
Hamill et al. (1986), continuing on the theory of Solomon et al. (1986), pointed out that reaction (12), as a gas phase reaction on the surface of a PSC particle, is a relatively slow reaction. However, if HCl and ClNO_3 were both in an aqueous state (HCl dissolved in a water droplet and ClNO_3 condensing into an aqueous aerosol), then reaction (12) would lead to a rapid production of Cl_2 and HNO_3 .

Toon et al. (1986) postulated that PSCs sequester large quantities of odd nitrogen from the lower stratosphere in the form of condensed HNO_3 . As mentioned above, chlorine chemistry is most effective in the depletion of ozone when low levels of NO_x are maintained. The slow downward displacement (sedimentation) of PSCs towards the end of winter could lead to the removal of odd

nitrogen from the lower stratosphere allowing the chlorine free radical to attack ozone catalytically.

However, Austin et al. (1986) have reported that LIMS data indicates virtually no PSCs at 20 km in the southern vortex after September 10, 1979. This absence of PSCs, and the associated heterogenous reactions would place more constraints on the chemical explanations for the ozone hole.

McElroy et al. (1986) have proposed an explanatory mechanism based upon the mutual interaction of BrO and ClO. If both chlorine and bromine are present in the stratospheric vortex in the form of their reactive oxides, ClO and BrO, then ozone concentrations can fall through the catalytic reactions:



Note that these reactions proceed in the absence of sunlight. Low levels of odd nitrogen are required to maintain the high concentrations of ClO, otherwise ClONO₂ will form. Thus, a mechanism, such as PSC sedimentation, is required to lower odd nitrogen levels.

While some investigators seek a photochemical solution to the problem, others (Tung et al., 1986; Mahlman and Fels, 1986; Rosenfield and Schoeberl, 1986; Bojkov, 1986;

Chandra and McPeters, 1986) believe that the dynamics of the Antarctic stratosphere play an important part in this seasonal depletion of ozone. As shown in Fig. 4, the mean lower stratospheric circulation normally takes the form of two diabatic cells with rising motion in the tropics and subsidence at the poles. Tung et al. (1986) were the first to propose a reversal in the circulation near the pole in which rising motions in the polar stratosphere would bring ozone-poor air from the lower layers to the stratosphere. Tung and his colleagues contend that during the south polar winter, dynamical transport of heat into the circumpolar vortex is so weak that radiative cooling approximately balances diabatic heating and the ambient temperature approaches radiative equilibrium. After the sun rises, absorption of solar radiation by ozone in the lower stratosphere leads to an increase in local heating. Since the radiation cooling to space is temperature sensitive, it remains close to the low values attained during the long polar night. However, the net heating offsets the radiative balance and rising motions result (Fig. 13). Tropospheric air with low ozone mixing ratios would then be brought into the lower stratosphere and thus, ozone concentrations would be reduced. This upward transport of ozone is thought to have a close relationship with the thermal structure of the stratosphere.

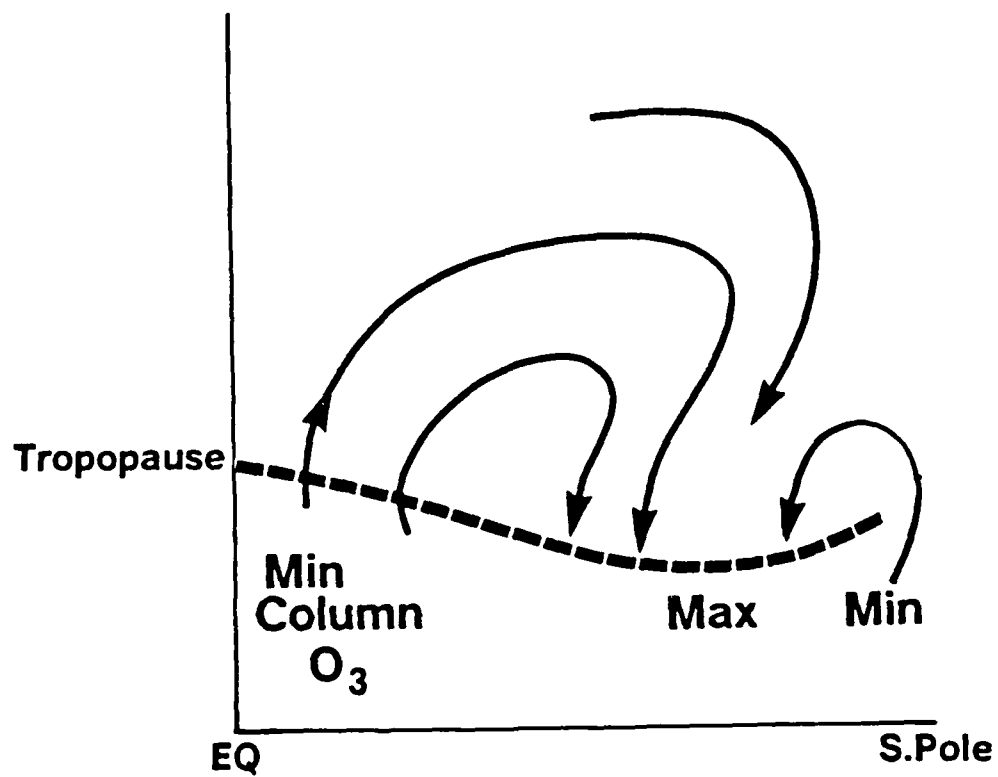


FIGURE 13. A schematic diagram depicting the reverse circulation (rising motion at the poles) theory of the ozone minimum at the South Pole.

Many investigators (Sekiguchi,1986;Chubachi and Kajiwara,1986;Newman and Schoeberl,1986;Angell,1986; Iwasaka and Kondoh,1986) believe a general cooling of the winter polar stratosphere has taken place with the decrease in total ozone. South polar October mean temperatures may have declined by as much as 18 K at 24 km over the last several years (Newman and Schoeberl,1986). Angell (1986) has noticed a 6-8 K decrease in the lower stratospheric temperature associated with the 30 percent depletion of ozone. In Fig. 14, interannual changes of 100 mb temperatures measured in November at Syowa, Antarctica are shown. The positive correlation between total ozone and lower stratospheric temperatures has been known since ozone observations first began (Meetham,1937). However, the depression of these temperatures is considered to be too large to result from the change in heating rates due to the depleted ozone levels observed in the lower stratosphere alone (Rosenfield and Schoeberl, 1986), but may be explained by the upward motions described by the reverse circulation theory. An upward circulation will produce adiabatic cooling of the stratosphere. (Newman and Schoeberl,1986).

Absorption of solar radiation by aerosols may enhance this upwelling of lower stratospheric air. Tung et al. (1986) believe that the current observed ozone depletion is a result of increased absorption of heat by the aerosol

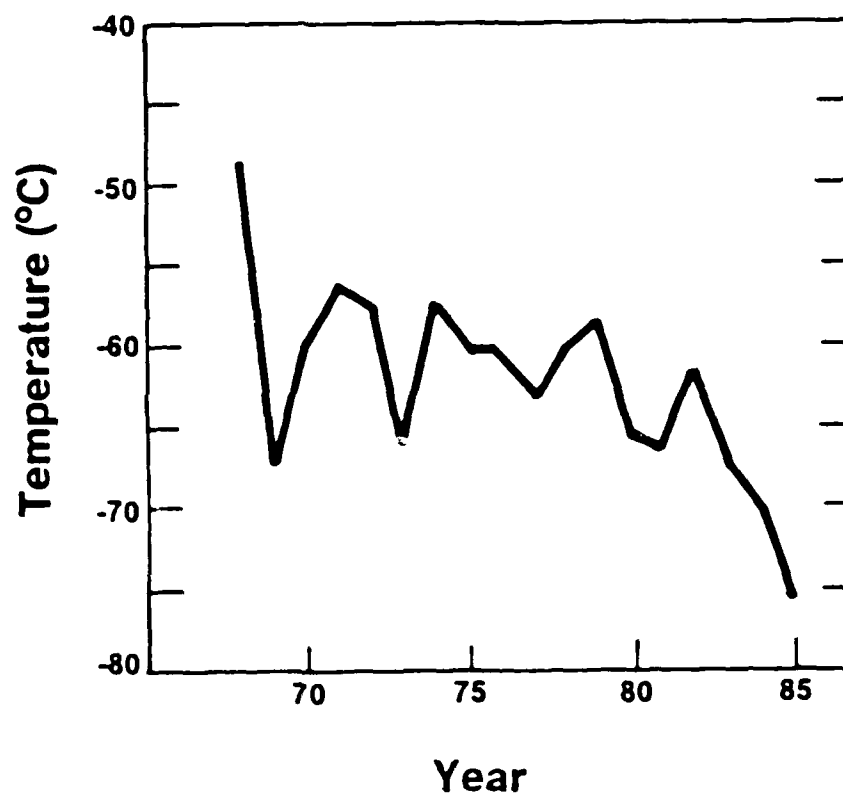


FIGURE 14. Interannual changes in 100 mb temperatures at Syowa, Antarctica in November.

loading of the Antarctic stratosphere. Aerosol loading had increased, principally from the El Chichon volcanic eruption of 1982. Although, stratospheric concentrations have been decreasing by a factor of two since 1983 (Hofman et al., 1986), the present levels are still much higher than pre-1982 levels (McCormick and Trepte, 1986). The additional absorption of heat by PSCs is also thought to enhance these rising air motions.

Mahlman and Fels (1986) propose that since 1979 there has been a substantial decrease in planetary wave activity and tropospheric forcing in the Southern Hemisphere. As a result, the stratospheric vortex is colder with stronger westerly winds, and thus maintains its integrity longer. Transport of ozone from lower latitudes is therefore delayed, and PSCs remain within the vortex until the sun rises. Since the ambient polar temperatures are near radiative equilibrium, absorption of heat by the PSCs, once the sun is up, initiates the necessary rising motions to bring ozone-poor air up from the troposphere. Mahlman and Fels (1986) roughly calculated vertical velocities of up to 50 m/day due to the absorption by PSCs. Rosenfield and Schoeberl (1986) simulated an upward polar vertical motion using a radiative transfer model. Their model suggests that the required upward motion within the vortex could be sustained if an additional heat source of at least 0.5 K/day could be provided. It is quite possible

that radiative absorption by PSCs and aerosols could provide this additional heat source.

The redistribution of ozone from the pole to mid-latitudes (Stolarski and Schoeberl, 1986) also tends to support the dynamical explanations. TOMS data revealed that the total amount of ozone south of about 44 S is conserved from August through November for any one year. Thus ozone appears to be transported up and away from the south polar and equatorial regions and move towards the mid-latitude region during the spring (Fig 13). However, the value of total ozone in this region has been decreasing from year to year.

Extraterrestrial phenomena producing catalytically attacking radicals are proposed as the basis for the third explanation of the ozone hole. Callis and Natarajan (1986) related the depletion of ozone to the sun's 11-year cycle and postulated that the depletion is principally due to catalytic destruction by growing odd nitrogen concentrations caused by increases in solar activity. They hypothesize that during periods of solar maxima, large amounts of NO_x are produced in the thermosphere, and are then transported through the mesosphere to the stratosphere during the polar night. Within the stratosphere, these concentrations are transported further downward, to altitudes of 25-30 km within the confines of the polar vortex of the Southern Hemisphere. During the

continuing downward motion within the stratosphere, the odd nitrogen of thermospheric and mesospheric origin is mixed with the odd nitrogen of stratospheric origin. During the long polar night, high levels of N_2O_5 and NO_3 are formed. After the sun rises, these molecules rapidly photodissociate producing NO and NO_2 to deplete the ozone.

Solar maximum for the current solar cycle (cycle 21) occurred in 1979 and Callis and Natarajan (1986) believe that the transport of odd nitrogen from the thermosphere to the lower stratosphere is very slow. They assume that the largest amounts of odd nitrogen produced by this cycle have finally, in 1985, reached the level of maximum concentrations of ozone in the lower stratosphere, producing the greatest effect on the ozone. Therefore, the next several years should see the odd nitrogen levels decrease and the springtime Antarctic ozone depletions not as severe as that in 1985. In contrast to the dynamical theories, Callis and Natarajan's theory requires that the stratospheric circulation maintains its diabatic downward motion over the southern pole.

Sekiguchi (1986) also suggests that the year to year change in south polar ozone and lower stratospheric temperatures results primarily from the influence of solar activity. Another extraterrestrial theory is that of Aikin and McPeters (1986) who theorize that the polar ozone perturbation is a result of increased levels of

chlorine which eventually develop in the lower stratosphere from the constant bombardment of meteoric atoms on the constituents of the mesosphere.

Ozone replenishment occurs in conjunction with both the sudden warmings of the stratosphere and the breakdown of the vortex in the period between mid-October and mid-November. During this period, the stratospheric circulation undergoes a transition from a winter to a summer pattern, the temperatures at 10 mb rise by as much as 20 K in four days, the circumpolar westerlies are replaced by easterlies (Farrara and Mechoso, 1986) and total ozone jumps up to its annual maximum value. Fig. 15 shows daily total ozone measurements from 10 October 1985 to 30 November 1985 at Amundsen-Scott, Antarctica (90S). From 10 October to 28 October, total ozone values were under 160 DU. At the onset of vortex breakdown, total ozone values climb to over 150 DU in less than a week (28 October - 4 November) due to transport from lower latitudes. During the rest of November, total ozone values fluctuate as transient waves, with different ozone content, move over the station.

6.3 Recent Observations

To observe the formation of the ozone hole, the National Ozone Expedition (NOZE) deployed to McMurdo Station, Antarctica in August 1986. Preliminary reports

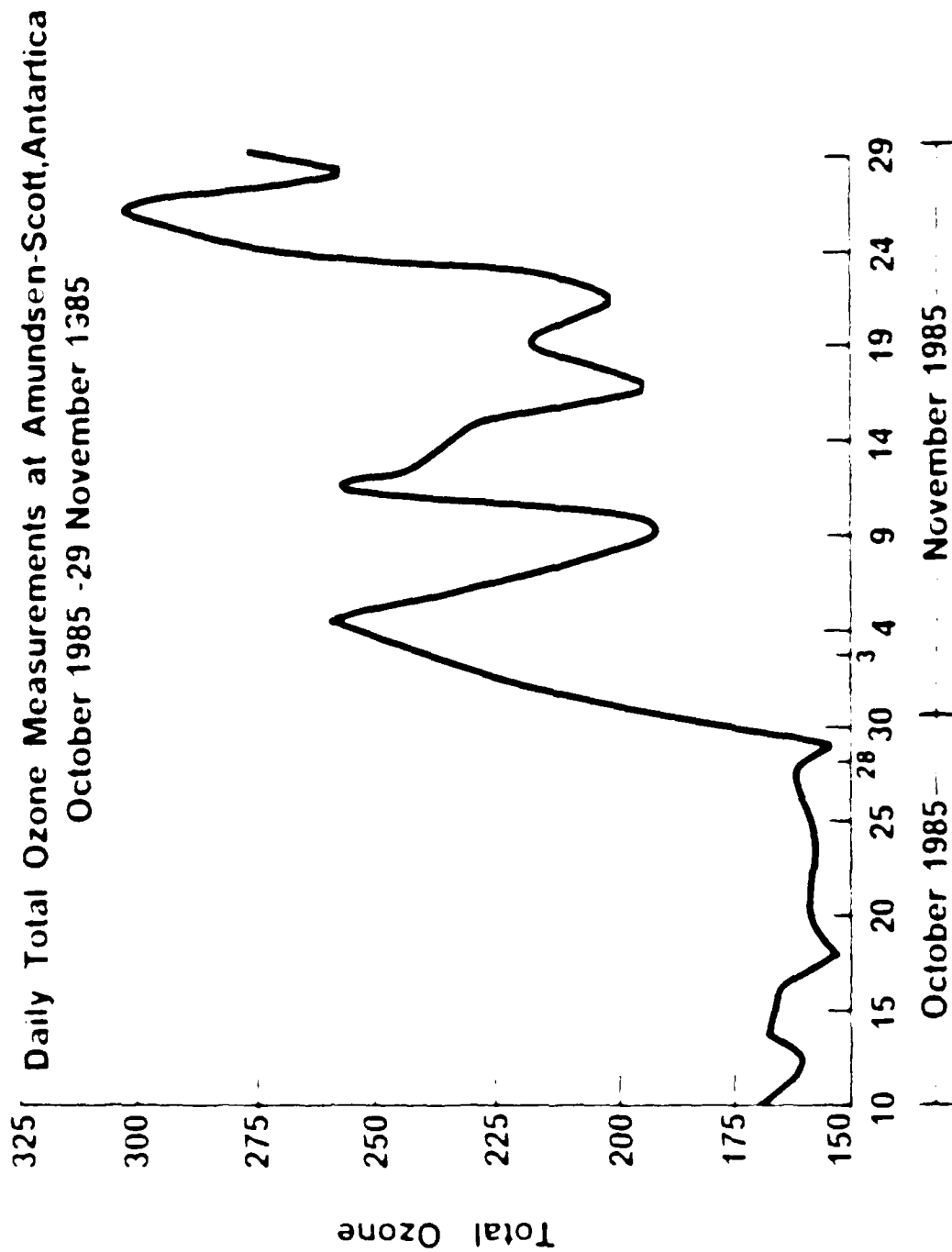


FIGURE 1

(2 October 1986 news release) stated that the observed depletion of 40 percent of the total ozone took place in 20 to 30 days. Balloonsonde data revealed fine vertical structure in the ozone mixing ratio profile, with large changes (20 to 80 percent) in ozone concentration taking place over height differences of a few hundred meters, and most of the depletion taking place at altitudes between 12 and 22 km (Margitan, 1987). This behavior would support the ozone depletion due to PSCs. However, it does not support the solar activity theory, which requires larger depletion at higher altitudes. Although, it should be noted that TIMS data has since revealed a second depletion region between 40 and 50 km (McPeters et al., 1986).

Measurements of trace gases by the NOZE team revealed that concentrations of NO and NO₂ are very low. In fact, the measurements are the lowest ever measured of these gases anywhere on earth. This finding also does not support the solar activity theory, but it is consistent with the chlorine catalysis theory. However, chlorine concentrations were also lower than expected (<1 ppbv). Since some models (Solomon et al., 1985) suggest chlorine concentrations between 0.5 to 1.0 ppbv, it would appear that chlorine chemistry is not the main mechanism.

The NOZE scientists also report the lack of any evidence needed to support the reverse circulation theory. Not only does the ozone deplete from high altitudes to

lower altitudes, vertical motions needed to support the theories were not observed. Dynamic models showed that upward motions of 0.02 cm/s (Rosenfield and Schoeberl, 1986; Mahinen and Fels, 1986) are needed to reproduce the ozone depletion levels observed. Therefore, dynamical mechanisms, as suggested by Tung et al. (1986), Mahinen and Fels (1986), and others appears to be inadequate to explain all of the observations currently obtained. Consideration of the dynamics of the Antarctic stratosphere cannot be ruled out, however, as it is generally agreed they play a critical role in establishing the unique conditions responsible for the ozone depletions.

CHAPTER VII

CONCLUSION

The Antarctic ozone hole problem is one of the most perplexing facing atmospheric scientists today. The process which forms the hole is still unknown. Many more measurements are needed throughout the continent of Antarctica. The NOAA observations were only at one location near the edge of the vortex so that their measurements may not be representative. If the depletion is due to photochemical effects, the decline in ozone would begin at the beginning of the polar day on the edge of the vortex. As the sun advances poleward, effects would spread into the vortex. A dynamical cause would suggest a change in the stratospheric circulation and a more even distribution of the changes in total ozone.

Depletion of the ozone in Antarctica need not be interpreted as a premonition of the destruction of the entire ozone layer. A chemical cause would most likely be confined to the unique conditions of the Antarctic stratosphere. Dynamical factors probably cause a redistribution of the ozone from the pole to mid-latitudes. Continued monitoring from the ground, air and space is necessary to have a better understanding of what is happening in the south polar spring. Already scheduled for next year is NASA's ER-2 high altitude research aircraft to gather in-situ samples of PSCs. No

doubt, a similar expedition to that of NOZE will also take place next year. It is imperative that the data obtained from NOZE be analyzed as quickly as possible so that revised theories of ozone depletion in Antarctica can be formulated, and relevant field experimental programs designed.

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National Aeronautics and Space Administration
Earth Science and Applications Division, Code EE
Washington, D.C. 20546.

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National Aeronautics and Space Administration
Earth Science and Applications Division, Code EE
Washington, D.C. 20546.

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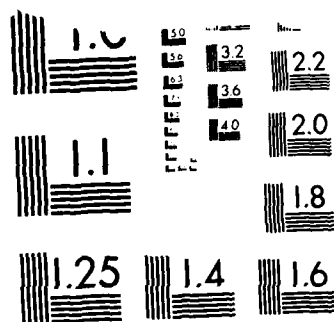
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